CHAPTER II
LITERATURE SURVEY

2.1 Microemulsion

Microemulsions, mixtures of oil, water and an amphiphile are thermodynamically stable and low viscosity. A phenomenon unique to surfactants is the self-assembly of molecules into dynamic clusters called micelles. Micelle formation occurs above a critical concentration of surfactant monomers, referred to as the critical micelle concentration (CMC), which is different for various surfactants. The center core of micelle acts as a dispersion phase. As an increasing amount of oil is added to the system at concentration of surfactant, the micelles continue to grow. The aggregate has properties similar to those of bulk oil. The phase separation will not occur and emulsions are thermodynamically stable.

Most technological applications of microemulsion use low molecular weight alcohol as a cosurfactant in formulation. The cosurfactant is mainly partitioned inside microemulsion phase. It permits the additional solubilization of large amount of unpolar liquid such as oil in water and is perhaps to prevent formation of rigid structures (e.g. gel, liquid crystals, precipitate). Shiao et al. (1998) found that it was necessary to add high alcohol content to stabilize microemulsion system with high oil/soap ratio. Sjoblom et al. (1996) investigated the effect of cosurfactant chain length and reported that the attraction between the aggregates increased when the alcohol chain length was decreased. Maidment et al. (1997) showed that addition of cosurfactant (pentanol) increased the range of stability of microemulsion toward higher total content of surfactant and cosurfactant. Trotta et al. (1998) reported the use of n-alkanol phosphocholines, as a cosurfactant, to form

microemulsion which was containing phosphatidylcholines (lecithin) as a surfactant for potential drug delivery systems that the formation of microemulsion depended on carbon chain length of alcohol and the size of microemulsion phase increased on increasing the length of the n-alkanol phosphocholines chain. Yao and Romsted (1997) studied 1-butanol (BuOH) to form the W/O cetyltrimethyl-ammonium bromide (CTABr) microemulsion with different types of oil and found that the bound fraction of BuOH was essentially independent of oil type in composition containing the same number of moles of each component, but the bound fraction increased with oil molecular weight at the same weight of CTABr, H_2O and oil soluble.

Many studies showed attempts to reduce or replace alcohol with other types of cosurfactant. Thevinin *et al.* (1997) reduced amount of alcohol used to prepare microemulsion system with sucrose oleate microemulsion system for pharmaceutical. Meziani *et al.* (1997) used an aldehyde as pentanal instead of alcohol cosurfactant. The ternary phase diagrams of water/SDS/aldehyde were determined and compared to the corresponding alcohol diagrams. The comparative study showed similarities between the aldehyde system and alcohol system. It can be assumed that alcohols and aldehydes have similar behavior. Sunwoo and Wade (1992) reported the minimization and possible elimination of cosurfactant from microemulsion formulations by optimizing surfactant structures. It was found that hydrophobe structure had a significant effect on cosurfactant requirements of the microemulsion system. When alkylamine was used as a cosurfactant in water, anionic surfactant, and oil microemulsion system, alkylamine brought about a sphere-to-rod transition in aqueous micellar solutions of cationic or anionic surfactants in the same way as long chain alcohols did. Backlund *et al.* (1997) studied the aggregation in alkanoic acid/alkylamine/water system which was known that acids and amines in an equimolecular ratio gave rise to cationic surfactant. The results of phase diagrams at 25 ^{O}C showed liquid

crystalline and two isotropic phases. Kahlweit *et al.* (1995) presented nontoxic microemulsions prepared by using an unsaturated fatty acid ethyl ester an as oil, a long chain soy bean lecithin as an amphiphile, and pentane-1,2-diol as a cosolvent. The mixture permitted the preparation of microemulsions at any prescribed temperature. Furthermore, Kahweit also prepared a nontoxic microemulsions by using isopropyl myristate/epikuron/c_5-diol/water.

Selle *et al.* (1991) investigated phase behavior and evaluated the stability of the emulsions system containing water (electrolyte)/sodium octanoate/octanoic acid/n-heptane without alcohol cosurfactant. Aorwiriyakul (1998) formed alcohol-free microemulsion system from the Dowfax8390/perchloroethylene (PCE)/octanoic acid. The result showed the enhancement of octanoic acid in producing the microemulsion for subsurface remediation.

2.2 Phase Behavior

Phase behavior studies are necessary for evaluating use of microemlsion systems. They provide information on the boundaries of the different phase as a function of composition, temperature, and more importantly structural organization can be also inferred (Kahlweit, 1995).

The phase behavior of multiphase microemulsions is found to change with surfactant concentration. These changes are reflected in the salinity requirement diagram, which decreases the variation in optimal salinity with surfactant concentration. Monovalent cations like sodium, show in some case an increase in the optimal salinity when the surfactant concentration is decrease (Aarra *et al.*, 1999).

Given the large number of components - five for oil, water, ionic surfactant, cosurfactant, and salt - complete phase diagrams would be

multidimensional and hard to draw or describe. Therefore one usually gives suitable cuts through the complete phase diagrams and/or one diminishes the number of components by combining for example water and salt into one quasi-component, brine.
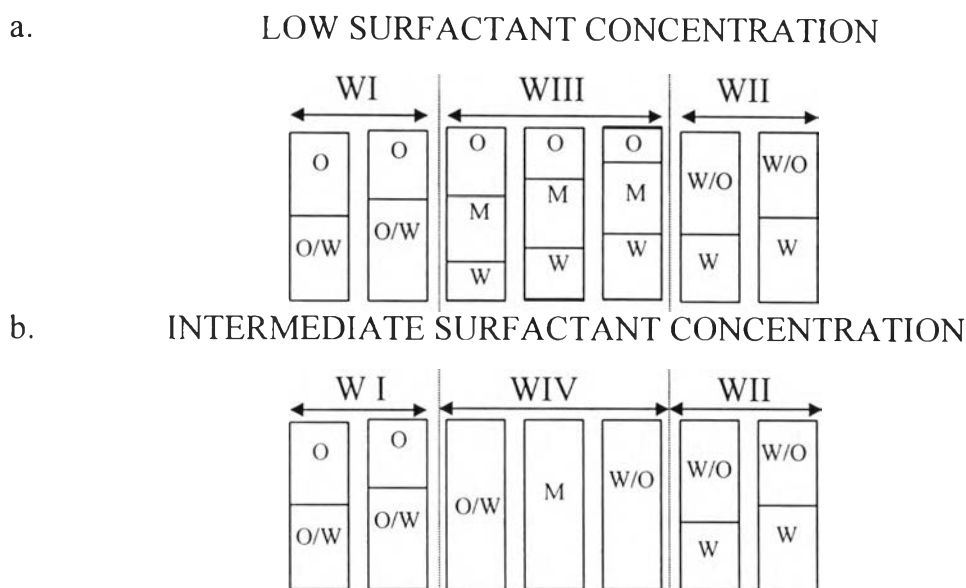
a.   LOW SURFACTANT CONCENTRATION

b.   INTERMEDIATE SURFACTANT CONCENTRATION

Figure 2.1 Schematic illustration of the progression of microemulsion phase equilibria prepared from equal volume of an aqueous phase (water, ionic surfactant, salt) and an oil phase (oil, cosurfactant) with increasing salinity

Figure 2.1 shows phase equilibria prepared from equal volumes of an aqueous phase (water, ionic surfactant, salt) and an oil phase (oil, cosurfactant). At low salt concentrations O/W microemulsions are found in equilibrium with excess oil; at high salt concentrations one finds W/O microemulsions plus an excess aqueous phase; in between three phase equilibria (W + microemulsion + O) occur at low amount of surfactant (Figure 2.1a), but one phase microemulsions at higher amount of surfactant (Figure 2.1b). In this study O/W microemulsion is classified as Winsor type I. A Winsor type III microemulsion, also named a middle phase microemulsion, is

defined to be W + microemulsion + O, and Winsor type II refers to a W/O microemulsion. Completely similar series of phase equilibria are found at constant concentration of salt but increasing concentrations of cosurfactant.

In addition, phase behavior studies allow comparison of the efficiency of different surfactants for a given application. The boundaries of one-phase regions can be assessed easily by visual observation of sample of known composition. However, long equilibration times in multiphase regions, especially if liquid crystalline phases are involved, can make this determination long and difficult.

2.3 Solubilization Parameter

When surfactant is added to the aqueous phase, the organic interior of micelles acts as an organic pseudophase into which organic contaminants can be partitioned. This phenomenon is called solubilization. In an aqueous system, the extent to which a solute will concentrate in a micelle can be related to the octanol-water partition coefficient (K_{ow}) of the solute (Edwards et al.,1991). In general, the larger the K_{ow} of a solute the greater will be its tendency to concentrate inside the micelle. Thus, micelles in a solution represent an increased capacity of the mobile aqueous phase for the organic solute over that of pure water. Enhanced solubility of contaminants has been described using a two-phase separation model for solute behavior.

The solbilization capacity of a middle phase microemulsion is a critical factor in selecting the preferred surfactant system. The term solubilization parameters (SP) were first introduced by Healy and Reed (1976)

$$SP_o = V_o/V_s \qquad\qquad (1a)$$

or $\qquad$ $SP_w = V_w/V_s$ $\qquad$ (1b)

where SP_o and SP_w are solubilization parameters for oil and water, respectively ; V_o and V_w are volumes of oil and water solubilized in the micellar solution, respectively; and V_s is the volume of surfactant in the micellar solution, excluding the cosurfactant volume (if used).

A modified oil solubilization parameter is used in this study. The solubilization power is defined per surfactant unit mass rather than per unit volume, as follows

$$SP_o = V_o/M_s \qquad (2)$$

where M_s is the total mass (moles) of surfactant present. In this definition alcohol mass is also excluded in calculation of M_s. However, when other surfactants are used as cosurfactants, they are included in calculating (Aorwiriyakul *et al.*, 1998).

Assuming a lower phase microemulsion type I, an increase in the salt concentration leads to the transition WI– WIII– WII. During the transition the solubilization parameter for oil SP_o will increase while SP_w decrease. At one point in the three-phase region, type III, the volume of oil in the microemulsion phase is equal to the volume of water in the microemulsion phase:

$$SP_o = SP_w = SP^* \qquad (3)$$

This point is referred to as an optimum point because of the fact that several physical properties attain either a maximum or a minimum at or near this point. Aarra *et al.* (1999) described the change in solubilization parameter for oil and water with increasing NaCl concentration for the SDS system. SP_w

decreased with increasing NaCl concentration while SP_o showed the opposite trend. When calculating the water and oil soubilization parameters, this study assumed that all the surfactant was retained in the microemulsion phase. The salt concentration corresponding to the situation where $V_o = V_w$ is called the optimal salt concentration or optimal salinity.

2.4 Interfacial Tension

One of the most fundamental properties of an oil-water system that forms microemulsions is the interfacial tension between the oil and water phases. During the process of microemulsion formation one phase breaks up into the maximum number of droplets. The diameter of these droplets depends on the interfacial area produced by the surfactant molecules.

Interfacial tension (IFT) at the liquid (non aqueous phases liquids, NAPLS) - liquid (water) interface has been studied for surfactant enhanced remidiation (West and Harwell, 1992) or trapping organic liquid. Design of a surfactant system for mobilization of a trapped phase thus begin with designing a system to create an ultralow interfacial tension, less than 10^{-3} dyne/cm. The IFT is reduced when the middle phase is formed, is minimized when approximately equal volumes of the organic chemical and water are used in forming the middle phase, and decrease as the solubilization parameter increase. Sharma and Shan (1985) reported that the minimum in ultralow interfacial tension occurred when the concentration of the surfactant monomer in aqueous phase was maximum. They also found that the higher the solubilization of brine or oil in the middle phase microemulsion, the lower the interfacial tension with the excess phase. It was observed that there was an optimal alcohol (co-surfactant) concentration which could solubilize the maximum amount of brine and also produced ultralow interfacial tension.

Bansal *et al.* (1980) reported that as the alcohol (cosurfactant) in the oil phase was depleted, further growth of water droplet would increase the interfacial tension at the oil/water interface due to an increase in the area per molecule and thus destabilized the microemulsion. The interfacial tension between the two separated phases increased with added water.

2.5 Electrical Conductivity

Electrical conductivity has been widely used to determine the nature of the continuous phase and to detect phase inversion phenomena. The distinction between O/W (high-conductivity) and W/O (low-conductivity) emulsions is quite straight forward. Meziani *et al.* (1997) measured the electrical conductivity for the ternary systems water/SDS/aldehyde as a function of the water concentration and compared them also to the corresponding alcohol systems. The conductivity was measured in the water concentration range for which the systems are monophasic. Both the alcohol and the alkanal curves are bell-shaped. The maximum of the conductivity being situated roughly at the same water concentration. The characteristic shapes discussed at small water concentration (the "inversed micellar zone") is that an increase of the water content leads to an increasing exchange of surfactants molecules between the micelle and hence to an increasing conductivity due to the increased mobility of the charged surfactant molecules. On the other hand, the addition of water dilutes the systems and therefore the concentration of conductivity species decreases. The influence of the chain length of the alcohol and aldehyde on the conductivity of SDS molecules can be explained by different flexibilities of the interfacial film constituted by the association either of SDS/alcohol or SDS/aldehyde. With increasing chain length of the alcohol or aldehyde the film become more rigid thus reducing the mobility of the SDS molecules in the film. Similar results have already been

obtained for pseudo-ternary alcohol microemulsion system and for other micellar liquid. A conductivities signal of a structural change from bicontinous to water-in-oil droplets for didodecyldimethylammonium bromide (DDAB) were measured by Maidment *et al.* (1997). It was reported that as surfactant concentration increased the percolation became less abrupt, but a decrease in conductivity with addition of water always remained as a vestige of this transition. The same trend was also observed by Bourel and Schechter (1998). They reported that micelles showed the intermediate state of electrical conductivity by decreasing gradually from Winsor I to Winsor III to Winsor II. They believed that the amount of oil and water in micelle solutions affected electrical resistivity. The low resistivity value occurred near Winsor I to Winsor III boundary and increased as oil content in micelle solution increased. In 1987, Kahlweit *et al.* (1987) showed the results of the corresponding conductivity measurements, using a conductivity cell with platinized electrode and a Wayne-Kerr auto balance. They reported the conductivity versus temperature in the three-phase body of the system. As one raises the temperature, conductivity increases slightly due to the increasing mobiltiy of the ions and decreases steeply to remain very low with further rising temperature. At constant temperature the electrical conductivity of the quinary systems increases due to increasing salinity. The electrical conductivity was also studied by Savelli *et al.* (1996). The conductive behavior of microemulsion keratin crytine systems was observed with variation of cosurfactant chain length. They reported the different behavior of n-pentanol from n-heptanol and n-decanol systems. In the n-pentanol system the conductivities reached high values and varied almost linearly as the water content increased. The conductivity values in the n-heptanol and n-decanol systems were three orders of magnitude lower than in the n-pentanol system and underwent monotonic variations as the water content increased. The results were described and analyzed by a population of percolating

microdroplets which would allow the reagent to concentrate within the aqueous core. In microemulsions with n-heptanol and n-decanol, the compositions corresponding to conductivity maxima could be considered as a transition locus separating a region of premicellar hydrated surfactant aggregated from a region of swollen spherical micelles.

However, the behavior of microemulsions is very complex. A sharp increase in conductivity in certain W/O microemulsion system is observed at low volume fraction. This behavior is interpreted as an indication of a "percolative behavior" or exchange of ions between droplets before the formation of bicontinuous structures. If the electrolyte concentration is kept at low values (10^{-2}-10^{-3} M), no effect on the structure is observed (Solan et $al.$, 1997).